

Search for quantum electronic dipoles in the dimerized κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl salt

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Abstract – The Mott insulator κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl consists of molecular dimers arranged on an anisotropic triangular lattice and develops a canted antiferromagnetic ground state. It has recently been suggested that this system features purely electronic ferroelectricity which requires an electric dipole moment. Optical spectroscopy clearly rules out charge imbalance in this system, which excludes the existence of quantum electric dipoles on the dimers and subsequently a dipolar spin coupling. We suggest that the prominent in-plane dielectric response in κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl is due to short-range discommensurations of the antiferromagnetic phase in the temperature range $30 < T < 50$ K, and domain wall relaxations at lower temperatures.

Introduction. – The interplay of electronic correlations and magnetic frustration causes various exotic ground states, such as Mott insulator and quantum spin liquid, that have drawn enormous attention in recent years [1, 2]. Examples are exotic quantum phases on kagome and honeycomb lattices explored in graphene and transition metal compounds, for instance [3–6]. The realization by organic conductors with triangular lattices turns out to be especially suitable because they can be nicely tuned by slight chemical and physical variations [7, 8]. The κ -(BEDT-TTF)₂X materials serve as prime examples in this regard, spanning from the Fermi-liquid metal $X = \text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ that superconducts below 12 K, to the first example of a spin-liquid system found in $X = \text{Cu}_2(\text{CN})_3$ despite the strong exchange interaction of $J = 250$ K within the triangular lattice [9, 10]. In this work we take a closer look at the Mott insulator $X = \text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ which shows canted-spin antiferromagnetic ordering, *i.e.*, weak ferromagnetism at temperatures below 30 K [11–14].¹

The structure of κ -phase materials based on the bis-(ethylenedithio)tetra-thiafulvalene (BEDT-TTF) molecule

consists of two-dimensional layers of dimers arranged in an anisotropic triangular lattice. In particular, κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl forms an orthorhombic two-layer system (anion layers in *ac*-plane, *b*-axis perpendicular to it) with four BEDT-TTF dimers per unit cell due to the tilting along the *a*-axis in opposite direction for adjacent layers, as displayed in Fig. 1 a) [15]. Conducting layers of cationic BEDT-TTF molecules are separated by essentially insulating anion sheets. The BEDT-TTF donors form face-to-face dimers which themselves are rotated by about 90° with respect to neighboring dimers, as sketched in Fig. 1 b).

With an average of half a hole per molecule, the common theoretical description of κ -structures considers each dimer as a single site (an effective half-filled band) and applies a Hubbard model with strong on-site Coulomb repulsion U . Although it has captured most of the physics [16, 17], this approach was put into question recently because dielectric measurements yield certain features in κ -(BEDT-TTF)₂Cu₂(CN)₃ [18, 19] and κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl [20] that are interpreted as ferroelectric response due to charge disproportionation within the dimers. Consequently Hotta proposed a dipolar-spin liquid [21] taking the quantum electric dipoles on the dimers

¹ Although first experiments showed antiferromagnetism below 45 K, all subsequent measurements revealed the antiferromagnetic ordering and canting in the temperature range 20 K–30 K.

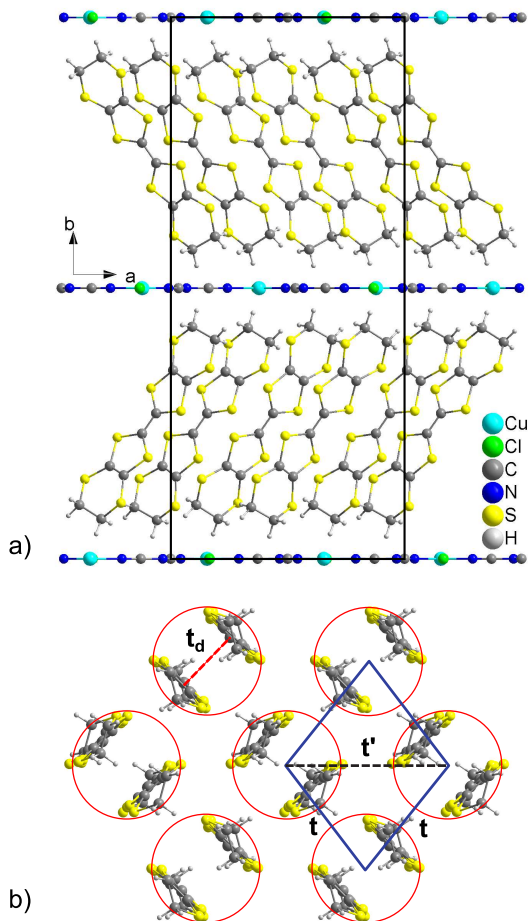


Fig. 1: (Color online) a) The side view on κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl demonstrates the staggered layers of BEDT-TTF molecules separated by sheets of polymeric anions. b) For κ -(BEDT-TTF)₂X in general, the molecules are arranged in dimers which constitute an anisotropic triangular lattice within the plane. The interdimer transfer integrals are labeled by *t* and *t'*, and intradimer by *t_d*.

into account that interact with each other through the dipolar spin coupling resulting in a quarter-filled two-band Hubbard model with intersite Coulomb interaction *V*. Similar considerations have been put forward by other groups [22,23]. Notably, a recent *ab initio* study of κ -phase materials applying a single-band extended Hubbard model [24] discovered that charge fluctuations are enhanced by the inter-dimer Coulomb interaction. Moreover, Tocchio *et al.* [25] showed that the magnetic phase can stabilize in presence of charge fluctuations. Here we present our dielectric and optical experiments on the dimerized κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl that are at odds with presented models. Our results call for reconsideration of the coupling between charge and spin degrees of freedom.

Experimental and Results. — Single crystals of the quasi-two-dimensional organic charge-transfer salt κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl (hereafter κ -Cl) were grown by standard electrochemical methods [26].

We revisit our ac measurements of complex conductivity on κ -Cl within the molecular planes $\mathbf{E} \parallel ac$ [13]. Complex dielectric spectra were obtained at temperatures 10–50 K by employing an LCR meter in the range 20 Hz–1 MHz. Two important improvements in data analysis have been implemented. First, stray-impedance background contributions of the sample holder have been measured in the open circuit configuration and subtracted from the sample measurements. To the resulting complex dielectric spectra $\varepsilon_{\parallel}(\omega)$ a sum of two generalized Debye functions was fitted, $\Delta\varepsilon_{\parallel,1}/[1 + (i\omega\tau_{0,1})^{1-\alpha_1}] + \Delta\varepsilon_{\parallel,2}/[1 + (i\omega\tau_{0,2})^{1-\alpha_2}] + \varepsilon_{\parallel,\text{HF}}$, where $\Delta\varepsilon_{\parallel}$ is the dielectric strength, τ_0 the mean relaxation time, $1 - \alpha$ the symmetric broadening of the relaxation time distribution function of the two dielectric relaxation modes, and $\varepsilon_{\parallel,\text{HF}}$ is the high-frequency dielectric constant. In particular, this approach successfully resolves the modes when they are near boundaries of the experimental frequency window. The second improvement extends the studied temperature range: above 30 K we determine the dielectric strength from capacitance measured between 10⁵ and 10⁶ Hz (well below the dielectric relaxation), which enables us to track the dielectric response up to 50 K. In the remainder of this paper we discuss in detail only the results obtained for Sample 2 of Ref. [13], which we consider quantitatively more reliable due to a negligible stray impedance after subtraction of background. An influence of other extrinsic effects, such as contact resistances and surface layer capacitances, was ruled out following the strict procedure explained in Ref. [27].

If the charge is unequally distributed among the molecules of the dimers, we may envision an electronic dipole moment within the layers. From our ac measurements on κ -Cl in the *ac*-plane we in fact see a very strong dielectric relaxational response [measured by the difference between static and high-frequency dielectric constant $\Delta\varepsilon_{\parallel} = \varepsilon_{\parallel}(0) - \varepsilon_{\parallel,\text{HF}} \approx 3000$] that emerges as the temperature drops below 50 K. The asymmetric shape of the dielectric function plotted in Fig. 2 clearly indicates the presence of two modes in the kHz range contributing with comparable strength. From the fits of $\varepsilon'_{\parallel}(\omega)$ and $\varepsilon''_{\parallel}(\omega)$ at a certain temperature we can extract their dielectric strength and mean relaxation time, shown in Figs. 3 a), b) as a function of $1/T$. The large error bars at 50 K reflect the difficulty in determining the modes at this temperature. At very low temperatures the dielectric strength of the first mode saturates at finite values of about $\Delta\varepsilon_{\parallel} \approx 300$, while the dielectric strength of mode 2 drops rapidly and eventually disappears at 7 K. The dielectric data on κ -Cl show that neither mode moves with temperature. The broadening parameter $1 - \alpha$ of modes 1 and 2 is 0.45 ± 0.05 and 0.80 ± 0.10 , respectively.

Recently Lunkenheimer *et al.* [20] measured the electric polarization switching and also the dielectric constant of κ -Cl perpendicular and parallel to the BEDT-TTF planes, the magnitude of latter comparable to our results. When

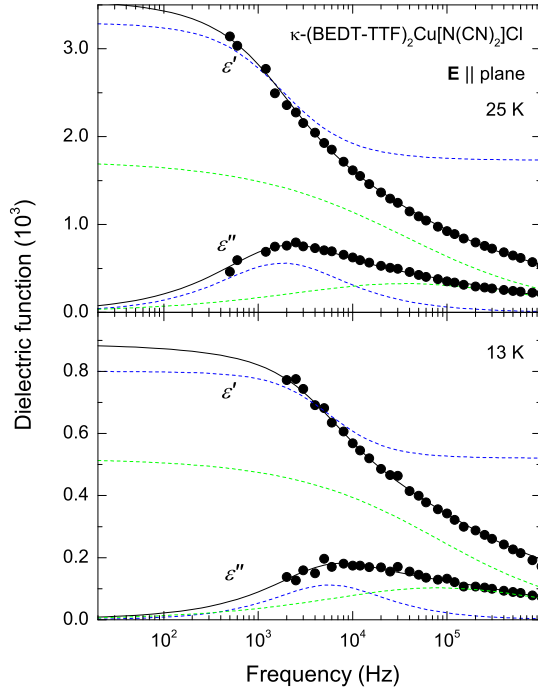


Fig. 2: (Color online) Real and imaginary parts of the in-plane dielectric function of κ -Cl at two temperatures ($T = 13$ K and 25 K). Full lines are fits to the sum of two modes, given by the green and blue dashed lines.

the temperature is reduced, the perpendicular dielectric constant peaks around 25 K. The maximum value increases for low frequencies up to $\epsilon'_{\perp}(\nu = 2.1 \text{ Hz}) \approx 420$. Since the dielectric anomaly occurs around the same temperature as magnetic ordering, they claim a loss of spin frustration due to ferroelectric ordering, resulting in antiferromagnetic spin order. However, a clear link of the magnetic order to the dielectric anomaly could not be presented. Most importantly, there is no experimental evidence of charge disproportionation on the dimers which is crucial for the ferroelectric interpretation.

In order to clarify this point, we have performed comprehensive in- and out-of-plane infrared measurements on κ -Cl single crystals down to 12 K. The frequencies of certain intramolecular vibration modes in BEDT-TTF crystals strongly depend on molecular charge, which makes Raman and infrared spectroscopy the superior local probe for the investigation of charge distribution [28–30]. Particular emphasis was put on the most charge-sensitive intramolecular vibrational modes $\nu_2(a_g)$, $\nu_3(a_g)$, and $\nu_{27}(b_{1u})$. The last involves the antisymmetric stretching vibration of the outer C=C bond as sketched in Fig. 4 and can only be observed perpendicular to the crystal plane. Measurements were taken on the thin sides of the crystals with 1 cm^{-1} resolution. Kramer-Kronig analysis was performed using a constant reflectivity extrapolation at low frequencies and temperatures.

In Fig. 4 the mid-infrared conductivity is plotted for different temperatures. Neighbouring the $\nu_{28}(b_{1u})$ doublet

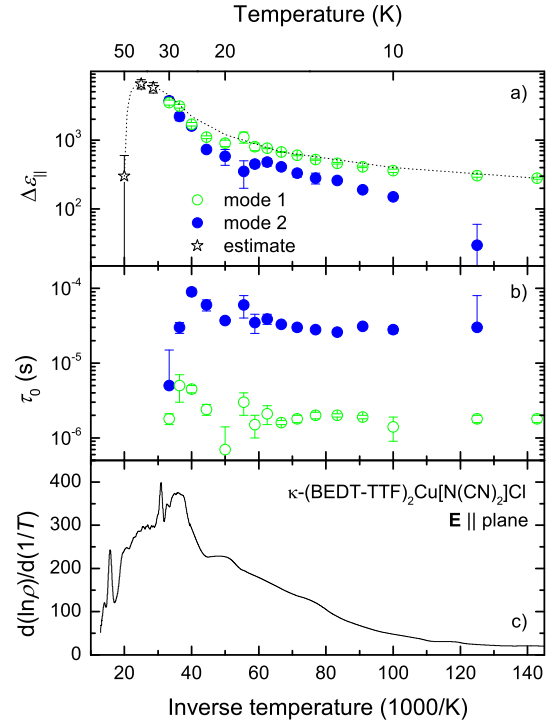


Fig. 3: (Color online) a) In-plane dielectric strength and b) mean relaxation time of κ -Cl as a function of inverse temperature. Empty green and full blue circles represent parameters of the mode 1 and mode 2, respectively. Above 30 K both modes are outside of the experimental frequency window and only the total dielectric strength $\Delta\epsilon_{||}$ can be extracted, denoted by stars. Dotted line is guide for the eye. c) The in-plane resistivity derivative shows a broad maximum which indicates the formation of a low-temperature phase at short-range scale. Dielectric response emerges in the region of resistivity crossover.

slightly above 1400 cm^{-1} , we observe the charge-sensitive $\nu_{27}(b_{1u})$ mode at 1460 cm^{-1} , where it is expected for half a hole per BEDT-TTF molecule [28, 29]. With decreasing temperature there is a slight hardening of a few cm^{-1} and a strong narrowing. In κ -Cl the molecules in adjacent layers are tilted in opposite directions as depicted in Fig. 1 a). The crystallographic inequality among the eight BEDT-TTF per unit cell causes two satellites to evolve at the high-frequency wing of the $\nu_{27}(b_{1u})$ mode.

The important observation is that the molecular vibrational modes do not split upon cooling, giving no indication of charge redistribution in κ -Cl as temperature is reduced. A similar conclusion can be drawn from the electron molecular-vibrational coupled totally-symmetric modes $\nu_2(a_g)$ and $\nu_3(a_g)$ [30]. According to the strong dependence of the eigenfrequency $\nu_{27}(b_{1u})$ on ionicity of -140 cm^{-1} per electron [28, 29], we can exclude a charge imbalance of more than 1% . A charge disproportionation of $\delta\rho = 0.6e$, typical for charge-ordered systems such as α -(BEDT-TTF)₂I₃ [31], results in a splitting of 80 cm^{-1} . Nothing like that is found, neither in our data [30], nor in temperature-dependent Raman and infrared experiments

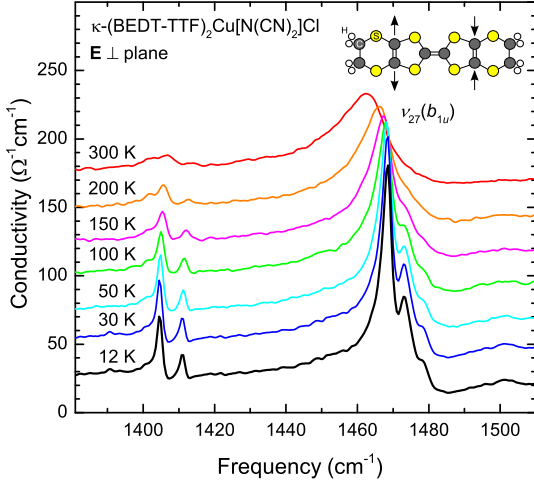


Fig. 4: (Color online) Temperature evolution of the out-of-plane optical conductivity of κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl measured at the narrow side of crystals. For clarity reasons the curves are shifted with respect to each other. Arrows on the sketched BEDT-TTF molecule indicate the antisymmetric C=C stretching vibrational mode $\nu_{27}(b_{1u})$ which is a very sensitive local probe of charge per molecule.

by other groups [28, 32]. κ -Cl becomes insulating due to Mott-Hubbard localization of one hole per BEDT-TTF dimer, rather than the formation of charge order.

Discussion. — The question now arises whether the dielectric relaxation observed in κ -Cl in and out of plane can be interpreted as a consequence of ferroelectricity, and in which way the theoretical model has to be modified. The ferroelectric approach very successfully describes commensurate charge ordering in the one-dimensional organic compounds (TMTTF) $_2X$, for which charge disproportionation was established by NMR and optical measurements [33]. Ferroelectricity becomes apparent in the divergence of dielectric constant at the transition temperature, where the two branches of $1/\Delta\epsilon_{\parallel}(T)$ above and below T_{CO} are very close to linear and the slope at $T < T_{CO}$ is two times larger than at $T > T_{CO}$. In two-dimensional electron systems, such as α -(BEDT-TTF) $_2$ I $_3$ or the ladder compound (Sr,Ca) $_{14}$ Cu $_{24}$ O $_{41}$, the situation is already quite different [27, 31, 34] in that no evidence for ferroelectric character of the CDW phase transition has been found. Indeed, the in-plane dielectric response in κ -Cl does not show this signature of ferroelectricity, either.

Let us consider the magnitude of ϵ , both in-plane and perpendicular to the molecular planes of κ -Cl. The out-of-plane dielectric response $\epsilon_{\perp} \approx 10 - 100$ [20] appears only for $T < 35$ K and is more than an order of magnitude smaller than ϵ_{\parallel} , which is present already below 50 K. These values of ϵ_{\perp} are typical for two-dimensional organic compounds [18, 35]. Previously, dielectric constants of $\epsilon_{\parallel} \approx 10^4$ and larger have been successfully attributed to the long-wavelength charge-order excitations, while $\epsilon_{\parallel} < 10^3$ is related to short-wavelength charge ex-

citations [13, 31, 34]; only the latter seem to be present in the κ -Cl system.

The data on κ -Cl evidence that a dielectric constant suddenly emerges below 50 K, reaches a maximum at $T_{cross} \approx 40$ K and decreases below. T_{cross} corresponds well to the broad maximum as shown by the in-plane resistivity derivative, Fig. 3 c). The appearance of dielectric response additionally coincides with the onset of the finite charge gap at 50 K and the enhancement of the antiferromagnetic spin correlations [36, 37]. Hence, the broad dielectric feature can be taken as an indication of a crossover into a new low-temperature phase which develops at short length scales. Nuclear magnetic and electron spin resonance measurements [12, 38–40] yield a weak ferromagnetic state below $T_N \approx 30$ K with substantial short-range fluctuations extending up to 60 K. Tanatar *et al.* proposed the formation of antiferromagnetic structure at temperatures as high as 70 K based on their observation of long-term (100 s) resistance relaxations both in Hall effect and magneto-resistance produced by a rotation of magnetic field [41]. This leads to the picture of magnetic domains which develop below 70 K and cause the metastable resistance across the domain walls due to soliton formation; the transient effects are largest at about 30 K and strongly drop below.

Associated with these domain walls, we suggest pairs of charged defects which respond to ac electric fields and carry spin as well as charge. While at elevated temperatures these are commensurate fluctuating antiferromagnetic domains, ferromagnetic domains develop at low temperatures. The dielectric mode 2 can thus be attributed to discommensurations of the otherwise commensurate antiferromagnetic phase which develops at short length scales below about 50 K. Once the antiferromagnetic phase with canted spins has formed at long scales (around 20 – 30 K) the dielectric response is taken over by domain walls of this ferromagnetic phase. The dielectric mode 1 then becomes the dominant contribution to the dielectric polarization at low temperatures. A similar conclusion can be drawn from the anisotropy of the dielectric constant that is considerable in the temperature region of antiferromagnetic fluctuations ($\epsilon_{\parallel}/\epsilon_{\perp} \geq 100$), but becomes much smaller ($\epsilon_{\parallel}/\epsilon_{\perp} \approx 5-10$) in the weak ferromagnetic state [20]. This effect happens at short length scales [42] but is not associated with macroscopic intra- and/or intermolecular distortions, as supported by infrared spectroscopy. Our findings are in line with theoretical consideration by Naka *et al.* [43] showing that magnetic and ferroelectric phases are exclusive to each other. In the end and in line with infrared results, no indication that points to a charge disproportionation was found in nuclear magnetic resonance data [44].

Conclusions. — Vibrational spectroscopy rules out any charge disproportionation in the dimerized κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl system with antiferromagnetic ground state and canted spins. No appreciable change in

the charge-sensitive vibrational features is revealed upon cooling, providing evidence that the charge distribution is not altered with decreasing temperature. The absence of electric dipoles on the dimers rules out ferroelectricity and is in accord with the low dielectric constant compared to known charge ordered systems [31]. The in-plane dielectric response of κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl is rather explained by short-range discommensurations of the anti-ferromagnetic phase in the temperature range 30 K < T < 50 K, and domain wall relaxations at lower temperatures. The weak dielectric response observed in the perpendicular direction is caused by the layered structure of these salts. Further theoretical efforts are needed to clarify the origin of dielectric relaxation observed in absence of charge disproportionation.

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